

# Evaluation of three-center two-electron repulsion integrals over Slater orbitals

Telhat ÖZDOĞAN<sup>†</sup> and María Belén RUIZ

Department of Theoretical Chemistry of the Friedrich-Alexander-University  
Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany

## Abstract

The Slater orbitals are the natural basis functions in quantum molecular calculations. Three-center repulsion Coulomb-exchange integrals over Slater orbitals are evaluated analytically with arbitrary orbital exponents, first for linear conformation of the atomic centers. These integrals have been expressed as a linear combination of three-center one-electron overlap integrals, and those have been calculated using auxiliary functions in terms of one-electron auxiliary integrals. Only one infinite expansion has been introduced. The resulting integral converges to 20 decimal digits using about 25-30 terms. Hybrid-exchange three-center repulsion integrals will be investigated next using this method, as well as triangular conformation of the centers.

**keywords:** Slater orbitals; three-center integrals; two-electron repulsion integrals

<sup>†</sup> Permanent address: Department of Physics, University of Rize, Turkey.  
This work has been supported by DFG and TUBITAK.

# 1. Introduction

Slater-type orbitals (STO) [1] are the natural basis functions in quantum molecular calculations. STOs represent well the electron density near the nucleus (cusp) and far from the nucleus (correct asymptotic decay). Therefore the STOs resemble the true orbitals. In contrast the Gaussian type-orbitals (GTO) show a wrong shape near and far of the nucleus (no cusp). Far of the nucleus the GTOs tend to zero much faster than STOs.

Nevertheless, the use of STOs was hindered in the last four decades by integration problems and the lack of a product theorem as in the case of GTOs. Consequently, Slater orbitals were replaced by Gaussian functions in molecular calculations [2]. Despite these difficulties the research on Slater orbitals has always continued. In 1982, in a Congress in Tallahassee about Slater orbitals Milan Randic described the situation: *"Gaussian functions are not the first choice in theoretical chemistry. They are used (...) primarily because molecular integrals can be evaluated, not because they possess desirable properties. Today this may be a valid reason for their use, but tomorrow they may be thought of as bastard surrogates, which served their purpose in the transition period, have no longer viable merits and will fail into oblivion"* [3]. The need of more accurate molecular Configuration Interaction (CI) calculations and Hartree-Fock (HF) calculations of large systems has resulted in the use of extremely large basis sets of Gaussian orbitals and dramatically expensive calculations.

The advantage of using Slater orbitals is that a single basis set would consist of one function per atom, what would shorten computational times. Also STOs would provide more accurate description of molecular properties where the density at the nucleus is important.

One of the main applications of STOs is the accurate calculation of energy and properties using the CI and Hylleraas-Configuration Interaction (Hy-CI) methods [4, 5]. For atoms and two-center molecules the necessary integrals are known. It would be desirable to extend the application of these methods to three-center molecules. We plan to test the integrals in the case of the  $H_3$  molecule and to use them in CI calculations of the  $BeH_2$  molecule.

As it is well-known there are no analytical general methods to calculate the three- and four-center integrals over Slater orbitals. This problem was soon recognized in early years (1959) by Mulliken and Roothaan, who called it *"The bottle-neck of Quantum Chemistry"* [6]. From the 90s until today many efforts have been made by several groups to develop efficient algorithms which have fructified in new computer programs for molecules. The bottle-neck of these programs is the calculation of the three- and four-center repulsion integrals. The approximate methods used are: one-center expansion [7, 8, 9, 10, 11], translation [12, 13], Gaussian expansion [14], Gauss transform [15, 16, 17], and Fourier transform [18, 19, 20, 21, 22, 23] methods. The disadvantages of these methods are on one hand side the low accuracy achieved, what results in longer expansions and increased computational times, and on the other side the need of numerical integrations. Recently, a special issue of a journal [24] and a book [25] are entirely dedicated to this topic. Also improvements of the translation [13], Fourier transform [23], and Gauss transform methods [17] to calculate the three-center repulsion integrals have been recently developed.

The purpose of this paper is to provide the formulas for the analytical evaluation of three-center overlap integrals. These integrals are important because the usual two-electron repulsion integral of the CI method can be expressed as a linear combination of three-center overlap ones. Therefore these overlap integrals should be calculated with high accuracy.

In 1936 Hirschfelder *et al.* [26, 27] solved some cases of two-electron repulsion integrals with

equal exponents of 1s-Slater orbitals in calculations of the  $H_3$  molecule. We have extended this method to different exponents, which is usually the case in quantum mechanical calculations. We will treat here the radial part of the integrals. The angular integration needs to be treated separately because the orientation of the angular functions depends on the geometry. Also the linear conformation of the centers will be studied first. In Appendix A we give some considerations for treating the symmetric triangular case.

Hybrid-exchange three-center repulsion integrals will be next investigated using this method.

## 2. Theory

We consider a linear three-center molecule, see Figure 1. The distances between the centers may be different and  $R = R_{ab} + R_{ac}$ . Let  $b$  and  $c$  be the focii of an ellipse, the atom  $a$  is placed along  $R$ . The elliptical coordinates of electron 1 are defined:

$$\mu_1 = \frac{(r_{1b} + r_{1c})}{R}, \quad \nu_1 = \frac{(r_{1b} - r_{1c})}{R}, \quad \phi_1 = \phi_1 \quad (1)$$

and the volume element is  $R^3/8(\mu^2 - \nu^2)d\mu d\nu d\phi$ . The coordinates of the center  $a$  are  $\mu_a = 1$ ,  $\nu_a = 0$  and  $\phi_a = 0$ . The distance between two points in elliptical coordinates is:

$$r_{1a}^2 = \frac{R^2}{4} (\mu_1^2 + \mu_a^2 + \nu_1^2 + \nu_a^2 - 2 - 2\mu_1\mu_a\nu_1\nu_a - [(\mu_1^2 - 1)(1 - \nu_1^2)(\mu_a^2 - 1)(1 - \nu_a^2)]^{1/2} \cos(\phi_1 - \phi_a)). \quad (2)$$

Substituting the coordinates of  $a$  in this equation we obtain:

$$r_{1a} = \frac{R}{2}(\mu_1^2 + \nu_1^2 - 1)^{1/2}, \quad (3)$$

The three-electron overlap integral over  $s$ -type Slater orbitals<sup>1</sup> is defined as:

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \int r_a^{n_a-1} e^{-\zeta_a r_a} r_b^{n_b-1} e^{-\zeta_b r_b} r_c^{n_c-1} e^{-\zeta_c r_c} d\tau, \quad (4)$$

where  $n_a, n_b, n_c$  are the principal quantum numbers of the three orbitals located in the centers  $a, b, c$ , and  $\zeta_a, \zeta_b, \zeta_c$  are the orbital exponents. In the following we will use the notation  $r_a = r_{1a}$ ,  $r_b = r_{1b}$ ,  $r_c = r_{1c}$ ,  $\mu_1 = \mu$  and  $\nu_1 = \nu$  because the integral depends only on one electron. Expressing  $r_b$  and  $r_c$  in elliptical coordinates with focii in  $b, c$ ,  $r_a$  is already given by Eq. (3):

$$r_b = \frac{R}{2}(\mu + \nu), \quad r_c = \frac{R}{2}(\mu - \nu) \quad (5)$$

Substituting Eqs. (3,5) in Eq. (4), writing explicitly the domains of integration and integrating over  $\phi$  we obtain:

---

<sup>1</sup>For simplicity only the radial integration will be performed here.

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \frac{2\pi R^{n_a+n_b+n_c}}{2^{n_a+n_b+n_c}} \int_1^\infty d\mu \int_{-1}^1 d\nu [(\mu^2 + \nu^2 - 1)^{1/2}]^{n_a-1} (\mu + \nu)^{n_b} (\mu - \nu)^{n_c} \times e^{-\alpha\mu - \beta\nu} e^{-\gamma(\mu^2 + \nu^2 - 1)^{1/2}}. \quad (6)$$

where the term  $(\mu^2 - \nu^2)$  from the volume element has been already included.  $\alpha$ ,  $\beta$  and  $\gamma$  are orbital exponents whose values are  $\alpha = R/2(\zeta_b + \zeta_c)$ ,  $\beta = R/2(\zeta_b - \zeta_c)$  and  $\gamma = R/2\zeta_a$ . Applying the Binomial Theorem in the form [28]:

$$(\mu + \nu)^m (\mu - \nu)^n = \sum_{k=0}^{m+n} D_k^{mn} \mu^{m+n-k} \nu^k, \quad (7)$$

and defining the coefficients  $D_k^{mn}$ :

$$D_k^{mn} = \sum_{\sigma} (-1)^{\sigma} C_{k-\sigma}^m C_{\sigma}^n, \quad C_{\sigma}^n = \frac{n!}{\sigma!(n-\sigma)!}, \quad (8)$$

we obtain:

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \frac{2\pi R^{n_a+n_b+n_c}}{2^{n_a+n_b+n_c}} \sum_{k=0}^{n_b+n_c} D_k^{n_b n_c} \int_1^\infty \mu^{n_b+n_c-k} e^{-\alpha\mu} d\mu \times \int_{-1}^1 \nu^k [(\mu^2 + \nu^2 - 1)^{1/2}]^{n_a-1} e^{-\beta\nu} e^{-\gamma(\mu^2 + \nu^2 - 1)^{1/2}} d\nu. \quad (9)$$

Now following Hirschfelder, Eyring and Rosen method [26], let us make the change of variable:

$$t = (\mu^2 + \nu^2 - 1)^{1/2} + \nu. \quad (10)$$

The limits are transformed as:  $\nu = 1 \rightarrow t = \mu + 1$  and for  $\nu = -1 \rightarrow t = \mu - 1$ . Defining  $b = \mu^2 - 1$ , we have:

$$\nu = \frac{1}{2} \left( t - \frac{b}{t} \right), \quad d\nu = \frac{1}{2} \left( 1 + \frac{b}{t^2} \right) dt. \quad (11)$$

Substituting Eq. (11) in Eq. (10):

$$(\mu^2 + \nu^2 - 1)^{1/2} = \frac{1}{2} \left( t + \frac{b}{t} \right), \quad (12)$$

and taking into account the transformation of the exponential part of Eq. (9):

$$e^{-\beta\nu} e^{-\gamma(t-\nu)} \rightarrow e^{-(\beta-\gamma)\nu} e^{-\gamma t} \rightarrow e^{-\frac{(\beta-\gamma)}{2} \left( t - \frac{b}{t} \right)} e^{-\gamma t} \rightarrow e^{-\frac{(\beta-\gamma)t}{2}} e^{-\gamma t} e^{\frac{\beta-\gamma}{2} \frac{b}{t}} \rightarrow e^{-\frac{(\beta+\gamma)t}{2}} e^{\frac{\beta-\gamma}{2} \frac{b}{t}}, \quad (13)$$

the three-center overlap integral is:

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \frac{2\pi R^{n_a+n_b+n_c}}{2^{n_a+n_b+n_c}} \sum_{k=0}^{n_b+n_c} \frac{1}{2^k} D_k^{n_b n_c} \int_1^\infty \mu^{n_b+n_c-k} e^{-\alpha\mu} d\mu \\ \times \int_{\mu-1}^{\mu+1} \left(t - \frac{b}{t}\right)^k \left(t + \frac{b}{t}\right)^{n_a-1} \left(1 + \frac{b}{t^2}\right) e^{-\frac{(\beta+\gamma)t}{2}} e^{\frac{\beta-\gamma}{2} \frac{b}{t}} dt, \quad (14)$$

where there is an exponential  $e^{-\gamma t}$  but also one exponential of the type  $e^{\frac{\beta-\gamma}{2} \frac{b}{t}}$ , difficult to integrate. Therefore we will use the following expansion which converges for a few terms of the series:

$$e^{\frac{\beta-\gamma}{2} \frac{b}{t}} \simeq \frac{1}{N!} \sum_{s=0}^N \frac{N!}{s!} \left(\frac{\beta-\gamma}{2} b\right)^s t^{-s}. \quad (15)$$

$N$  is the number of terms of the truncated expansion. Eq. (15) is the only infinite expansion introduced in the evaluation of the integral. Using the Binomial Theorem:

$$\left(t - \frac{b}{t}\right)^k \left(t + \frac{b}{t}\right)^{n_a-1} \left(1 + \frac{b}{t^2}\right) = \frac{1}{t} \left(t + \frac{b}{t}\right)^{n_a} \left(t - \frac{b}{t}\right)^k = \sum_{u=0}^{n_a+k} D_u^{n_a k} t^{n_a+k-2u-1} b^u, \quad (16)$$

we get the integral:

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \frac{2\pi R^{n_a+n_b+n_c}}{2^{n_a+n_b+n_c}} \frac{1}{N!} \sum_{k=0}^{n_b+n_c} \sum_{u=0}^{n_a+k} \sum_{s=0}^N \frac{N!}{s! 2^k} D_k^{n_b n_c} D_u^{n_a k} \left(\frac{\beta-\gamma}{2}\right)^s \\ \times \int_1^\infty \mu^{n_b+n_c-k} (\mu^2 - 1)^{u+s} e^{-\alpha\mu} d\mu \\ \times \int_{\mu-1}^{\mu+1} t^{n_a+k-2u-s-1} e^{-\frac{(\beta+\gamma)t}{2}} dt, \quad (17)$$

which can be expressed in terms of auxiliary integrals:

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \frac{1}{N!} \sum_{k=0}^{n_b+n_c} \sum_{u=0}^{n_a+k} \sum_{s=0}^N \frac{\pi N!}{2^{n_a+n_b+n_c+k-1} s!} D_k^{n_b n_c} D_u^{n_a k} \left(\frac{\beta-\gamma}{2}\right)^s \\ \times B_{n_b+n_c-k, s+u; n_a+k-2u-s-1} \left(\alpha, \frac{(\beta+\gamma)}{2}\right), \quad (18)$$

where  $B_{nm;\pm k}(\alpha, \beta)$  are auxiliary integrals, which will be treated in next the Section.

### 3. The auxiliary function $B_{nm;\pm k}(\alpha, \beta)$

We have expressed the three-center overlap integrals as a sum of auxiliary integrals  $B_{nm;\pm k}(\alpha, \beta)$  which are defined:

$$B_{nm;\pm k}(\alpha, \beta) = \int_1^\infty \mu^n (\mu^2 - 1)^m e^{-\alpha\mu} d\mu \int_{\mu-1}^{\mu+1} t^{\pm k} e^{-\beta t} dt. \quad (19)$$

Two cases are distinguished:  $k$  is positive  $t^k$  and the case  $t^{-k}$ . The corresponding indefinite integrals are [29]:

$$\int t^k e^{-\beta t} dt = -e^{-\beta t} \sum_{h=0}^k \frac{k!}{(h-k)!} \frac{t^{k-h}}{\beta^{h+1}}, \quad k \geq 0 \quad (20)$$

and

$$\int \frac{e^{-\beta t}}{t^k} dt = -e^{-\beta t} \sum_{h=1}^{k-1} \frac{(k-h-1)!}{(k-1)!} \frac{(-\beta)^{h-1}}{t^{k-h}} + \frac{(-\beta)^{k-1}}{(k-1)!} Ei(-\beta t). \quad k > 0 \quad (21)$$

We evaluate now the auxiliary function  $B_{nm;+k}(\alpha, \beta)$  for  $k \geq 0$  for the actual limits:

$$\int_{\mu-1}^{\mu+1} t^k e^{-\beta t} dt = \sum_{h=0}^k \frac{k!}{(h-k)!} \beta^{-h-1} [(\mu-1)^{k-h} e^{-\beta(\mu-1)} - (\mu+1)^{k-h} e^{-\beta(\mu+1)}] \quad (22)$$

substituting in Eq. (19),

$$\begin{aligned} B_{nm;+k}(\alpha, \beta) &= \sum_{h=0}^k \frac{k!}{(h-k)!} \beta^{-h-1} \left( e^\beta \int_1^\infty \mu^n (\mu+1)^m (\mu-1)^{m+k-h} e^{-(\alpha+\beta)\mu} d\mu \right. \\ &\quad \left. - e^{-\beta} \int_1^\infty \mu^n (\mu+1)^{m+k-h} (\mu-1)^m e^{-(\alpha+\beta)\mu} d\mu \right). \end{aligned} \quad (23)$$

The integration over  $\mu$  can be written as an one-electron auxiliary integral which is well-known:

$$B_{nm;+k}(\alpha, \beta) = \sum_{h=0}^k \frac{k!}{(h-k)!} \beta^{-h-1} (e^\beta A_{n;m,m+k-h}(\alpha + \beta) - e^{-\beta} A_{n;m+k-h,m}(\alpha + \beta)), \quad (24)$$

with

$$A_{n,mk}(\alpha) = \int_1^\infty \mu^n (\mu+1)^m (\mu-1)^k e^{-\alpha\mu} d\mu = \sum_{j=0}^{m+k} D_j^{mk} A_{n+m+k-j}(\alpha). \quad (25)$$

In the case of negative  $k$  the calculation is messier:

$$\begin{aligned} \int_{\mu-1}^{\mu+1} \frac{e^{-\beta t}}{t^k} dt &= \frac{(-\beta)^{k-1}}{(k-1)!} [Ei(-\beta(\mu+1)) - Ei(-\beta(\mu-1))] \\ &\quad - \sum_{h=1}^{k-1} \frac{(k-h-1)!}{(k-1)!} (-\beta)^{h-1} \left[ \frac{e^{-\beta(\mu+1)}}{(\mu+1)^{k-h}} - \frac{e^{-\beta(\mu-1)}}{(\mu-1)^{k-h}} \right], \end{aligned} \quad (26)$$

the auxiliary integral is then:

$$\begin{aligned}
B_{nm;-k}(\alpha, \beta) = & \frac{(-\beta)^{k-1}}{(k-1)!} \left[ \int_1^\infty \mu^n (\mu^2 - 1)^m e^{-\alpha\mu} Ei(-\beta(\mu+1)) d\mu \right. \\
& \left. - \int_1^\infty \mu^n (\mu^2 - 1)^m e^{-\alpha\mu} Ei(-\beta(\mu-1)) d\mu \right] \\
& - \sum_{h=1}^{k-1} \frac{(k-h-1)!}{(k-1)!} (-\beta)^{h-1} \left[ \int_1^\infty \mu^n (\mu^2 - 1)^m e^{-\alpha\mu} \frac{e^{-\beta(\mu+1)}}{(\mu+1)^{k-h}} d\mu \right. \\
& \left. - \int_1^\infty \mu^n (\mu^2 - 1)^m e^{-\alpha\mu} \frac{e^{-\beta(\mu-1)}}{(\mu-1)^{k-h}} d\mu \right], \quad (27)
\end{aligned}$$

simplifying:

$$\begin{aligned}
B_{nm;-k}(\alpha, \beta) = & \frac{(-\beta)^{k-1}}{(k-1)!} \sum_{i=0}^m (-1)^i C_i^m \left[ \int_1^\infty \mu^{n+2m-i} e^{-\alpha\mu} Ei(-\beta(\mu+1)) d\mu \right. \\
& \left. - \int_1^\infty \mu^{n+2m-i} e^{-\alpha\mu} Ei(-\beta(\mu-1)) d\mu \right] \\
& - \sum_{h=1}^{k-1} \frac{(k-h-1)!}{(k-1)!} (-\beta)^{h-1} \left[ e^{-\beta} \int_1^\infty \mu^n (\mu+1)^{m-k+h} (\mu-1)^m e^{-(\alpha+\beta)\mu} d\mu \right. \\
& \left. - e^\beta \int_1^\infty \mu^n (\mu+1)^m (\mu-1)^{m-k+h} e^{-(\alpha+\beta)\mu} d\mu \right]. \quad (28)
\end{aligned}$$

Finally:

$$\begin{aligned}
B_{nm;-k}(\alpha, \beta) = & \frac{(-\beta)^{k-1}}{(k-1)!} \sum_{i=0}^m (-1)^i C_i^m \left[ T_{n+2m-2i}^{(+)}(\alpha, \beta) - T_{n+2m-2i}^{(-)}(\alpha, \beta) \right] \\
& - \sum_{h=1}^{k-1} \frac{(k-h-1)!}{(k-1)!} (-\beta)^{h-1} \left[ e^{-\beta} A_{n;m-k+h,m}(\alpha+\beta) - e^\beta A_{n;m,m-k+h}(\alpha+\beta) \right] \quad (29)
\end{aligned}$$

the auxiliary integral for negative values of  $k$  is a sum of one-electron auxiliary integrals  $A_{n;mk}(\alpha+\beta)$  and a new kind of auxiliary integrals, which will be evaluated in the next Section.

### 3.1 Calculation of $\mathbf{T}_n^{(+)}(\alpha, \beta)$ and $\mathbf{T}_n^{(-)}(\alpha, \beta)$

The auxiliary functions  $T_{n+2m-2i}^{(+)}(\alpha, \beta)$  and  $T_{n+2m-2i}^{(-)}(\alpha, \beta)$  need to be calculated. They are defined as:

$$\begin{aligned}
T_n^{(+)}(\alpha, \beta) &= \int_1^\infty \mu^n e^{-\alpha\mu} Ei(-\beta(\mu+1)) d\mu, \\
T_n^{(-)}(\alpha, \beta) &= \int_1^\infty \mu^n e^{-\alpha\mu} Ei(-\beta(\mu-1)) d\mu.
\end{aligned} \quad (30)$$

The auxiliary functions  $T_n^{(+)}(\alpha, \beta)$  can be calculated using recursion relations. The first term is:

$$T_0^{(+)}(\alpha, \beta) = \int_1^\infty e^{-\alpha\mu} Ei(-\beta(\mu+1)) d\mu. \quad (31)$$

The higher terms can be calculated using the differential equation:

$$T_n^{(+)}(\alpha, \beta) = (-1)^n \frac{d^n}{d\alpha^n} T_0^{(+)}(\alpha, \beta). \quad (32)$$

Let us first solve  $T_0^{(+)}(\alpha, \beta)$ , making the change of variables:

$$\beta(\mu+1) = y, \quad \beta d\mu = dy, \quad \mu = \frac{y}{\beta} - 1, \quad (33)$$

the integration limits of the domains are transformed  $\mu = 1 \rightarrow y \Rightarrow 2\beta$  and  $\mu \rightarrow \infty \Rightarrow y \rightarrow \infty$ . To calculate  $T_0^{(+)}(\alpha, \beta)$  one has to solve the integral:

$$T_0^{(+)}(\alpha, \beta) = \int_{2\beta}^\infty \frac{1}{\beta} e^{-\alpha(\frac{y}{\beta}-1)} Ei(-y) dy. \quad (34)$$

Using the integration formula:

$$\int_c^\infty \frac{1}{\beta} e^{-\gamma y} Ei(-y) dy = \frac{1}{\gamma} [Ei(-c) e^{-\gamma c} - c Ei(-(\gamma+1))], \quad (35)$$

we have

$$T_0^{(+)}(\alpha, \beta) = \frac{e^\alpha}{\beta} \frac{1}{(\alpha/\beta)} \left[ Ei(-2\beta) e^{-\frac{\alpha}{\beta} 2\beta} - Ei\left(-\left(\frac{\alpha}{\beta} + 1\right) 2\beta\right) \right], \quad (36)$$

and simplifying:

$$T_0^{(+)}(\alpha, \beta) = \frac{e^{-\alpha}}{\alpha} Ei(-2\beta) - \frac{e^\alpha}{\alpha} Ei(-2(\alpha + \beta)). \quad (37)$$

The  $n$ th-term is:

$$T_n^{(+)}(\alpha, \beta) = (-1)^n \frac{d^n}{d\alpha^n} \left( \frac{e^{-\alpha}}{\alpha} Ei(-2\beta) - \frac{e^\alpha}{\alpha} Ei(-2(\alpha + \beta)) \right). \quad (38)$$

Let us use the Leibnitz formula:

$$\frac{d^n}{dx^n} (f(x)g(x)) = \sum_{m=0}^n C_m^n \frac{d^{n-m}}{dx^{n-m}} f(x) \frac{d^m}{dx^m} g(x) \quad (39)$$

calculating  $\frac{d^n}{dx^n} \frac{e^{-\alpha}}{\alpha} Ei(-2\beta)$  and  $\frac{d^n}{dx^n} \frac{e^\alpha}{\alpha} Ei(-2(\alpha + \beta))$ :

$$(-1)^n \frac{d^n}{d\alpha^n} \frac{e^{-\alpha}}{\alpha} Ei(-2\beta) = (-1)^n \frac{d^n}{d\alpha^n} (A_0(\alpha) Ei(-2\beta)) = A_n(\alpha) Ei(-2\beta) \quad (40)$$

and



$$\begin{aligned}
(-1)^n \frac{d^n}{d\alpha^n} \frac{e^\alpha}{\alpha} Ei(-2(\alpha + \beta)) &= (-1)^n \frac{d^n}{d\alpha^n} (-A_0(-\alpha) Ei(-2(\alpha + \beta))) \\
&= (-1)^{n+1} \sum_{m=0}^n C_m^n \frac{d^{n-m}}{d\alpha^{n-m}} A_0(-\alpha) \frac{d^m}{d\alpha^m} Ei(-2(\alpha + \beta)) \\
&= -A_n(-\alpha) Ei(-2(\alpha + \beta)) + \sum_{m=1}^n (-1)^{n-m} C_m^n A_{n-m}(-\alpha) Ei(-2(\alpha + \beta)). \quad (41)
\end{aligned}$$

We have used the following definitions of the exponential integral:

$$Ei(-z) = \int_{-\infty}^z \frac{e^{-t}}{t} dt = - \int_z^{\infty} \frac{e^{-t}}{t} dt \quad (42)$$

$$E_1(-z) = \int_z^{\infty} \frac{e^{-t}}{t} dt = -Ei(-z) \equiv Ei(1, z). \quad (43)$$

The derivatives of the exponential integral are

$$\frac{d}{d\alpha} Ei(-2(\alpha + \beta)) = (-1)(-2) \int_1^{\infty} e^{-2(\alpha+\beta)t} dt = 2A_0(2(\alpha + \beta)), \quad (44)$$

$$\frac{d^m}{d\alpha^m} Ei(-2(\alpha + \beta)) = \frac{d^{m-1}}{d\alpha^{m-1}} 2A_0(2(\alpha + \beta)) = (-1)^{m-1} 2^m A_{m-1}(2(\alpha + \beta)) \quad (45)$$

$$\begin{aligned}
(-1)^n \frac{d^n}{d\alpha^n} \left( \frac{e^\alpha}{\alpha} Ei(-2(\alpha + \beta)) \right) &= -(-1)^n A_n(-\alpha) Ei(-2(\alpha + \beta)) \\
&\quad + \sum_{m=1}^n (-1)^{n-m} 2^m C_m^n A_{n-m}(-\alpha) (-1)^{m-1} A_{m-1}(2(\alpha + \beta)). \quad (46)
\end{aligned}$$

Finally we have:

$$\begin{aligned}
T_n^{(+)}(\alpha, \beta) &= A_n(-\alpha) Ei(-2\beta) + (-1)^n A_n(-\alpha) Ei(-2(\alpha + \beta)) \\
&\quad - \sum_{m=1}^n (-1)^{n-m} 2^m C_m^n A_{n-m}(-\alpha) (-1)^{m-1} A_{m-1}(2(\alpha + \beta)) \quad (47)
\end{aligned}$$

To calculate the auxiliary functions  $T_n^{(-)}(\alpha, \beta)$  defined as:

$$T_n^{(-)}(\alpha, \beta) = \int_1^{\infty} \mu^n e^{-\alpha\mu} Ei(-\beta(\mu - 1)) d\mu \quad (48)$$

we use also recursion relations. Let us calculate also  $T_0^{(-)}(\alpha, \beta)$  defined as:

$$T_0^{(-)}(\alpha, \beta) = \int_1^{\infty} e^{-\alpha\mu} Ei(-\beta(\mu - 1)) d\mu. \quad (49)$$

The following change of variable is done:

$$\begin{aligned} u &= Ei(-\beta(\mu-1)), & \Rightarrow du &= \frac{e^{-\beta(\mu-1)}}{(\mu-1)} \\ dv &= e^{-\alpha\mu}, & \Rightarrow v &= -\frac{e^{-\alpha\mu}}{\alpha}. \end{aligned} \quad (50)$$

The integral  $T_0^{(-)}(\alpha, \beta)$  is the limit:

$$T_0^{(-)}(\alpha, \beta) = \lim_{\gamma \rightarrow 1} \int_{\gamma}^{\infty} e^{-\alpha\mu} Ei(-\beta(\mu-1)) d\mu, \quad (51)$$

integrating by parts:

$$T_0^{(-)}(\alpha, \beta) = \lim_{\gamma \rightarrow 1} \left( -\frac{1}{\alpha} e^{-\alpha\mu} Ei(-\beta(\mu-1)) + \frac{1}{\alpha} \int_{\gamma}^{\infty} e^{-\alpha\mu} \frac{e^{-\beta(\mu-1)}}{(\mu-1)} d\mu \right) \quad (52)$$

making again a change of variables, in this case:  $\mu-1 = u \Rightarrow d\mu = du$  and  $\mu = \gamma \Rightarrow u = \gamma-1$  with  $\mu \rightarrow \infty \Rightarrow u \rightarrow \infty$ , we have:

$$\begin{aligned} T_0^{(-)}(\alpha, \beta) &= \lim_{\gamma \rightarrow 1} \left( -\frac{1}{\alpha} e^{-\alpha\mu} Ei(-\beta(\mu-1)) + \frac{e^{-\alpha}}{\alpha} \int_{\gamma-1}^{\infty} \frac{e^{-(\alpha+\beta)u}}{u} du \right) \\ &= \frac{e^{-\alpha}}{\alpha} \lim_{\gamma \rightarrow 1} (Ei(-\beta(\mu-1)) - Ei(-(\alpha+\beta)(\mu-1))) \\ &= \lim_{\gamma \rightarrow 1} \left( -\int_{\beta(\gamma-1)}^{\infty} \frac{e^{-t}}{t} dt + \int_{(\alpha+\beta)(\gamma-1)}^{\infty} \frac{e^{-t}}{t} dt \right), \end{aligned} \quad (53)$$

using the identity

$$-\int_a^{\infty} \frac{e^{-t}}{t} dt = \int_a^1 \left( \frac{1-e^{-t}}{t} \right) dt - \int_1^{\infty} \frac{e^{-t}}{t} dt - \int_a^1 \frac{dt}{t} \quad (54)$$

and the definition of the Euler constant  $C$ :

$$C = \int_a^1 \left( \frac{1-e^{-t}}{t} \right) dt - \int_1^{\infty} \frac{e^{-t}}{t} dt = 0.5772156649015. \quad (55)$$

we get:

$$\begin{aligned} T_0^{(-)}(\alpha, \beta) &= \frac{e^{-\alpha}}{\alpha} \lim_{\gamma \rightarrow 1} \left\{ \int_{\beta(\gamma-1)}^1 \frac{1-e^{-t}}{t} dt - \int_1^{\infty} \frac{e^{-t}}{t} dt - \int_{\beta(\gamma-1)}^1 \frac{dt}{t} - \int_{(\alpha+\beta)(\gamma-1)}^{\infty} \frac{1-e^{-t}}{t} dt \right. \\ &\quad \left. + \int_1^{\infty} \frac{e^{-t}}{t} dt + \int_{(\alpha+\beta)(\gamma-1)}^1 \frac{e^{-t}}{t} dt \right\} \end{aligned} \quad (56)$$

$$T_0^{(-)}(\alpha, \beta) = \frac{e^{-\alpha}}{\alpha} \lim_{\gamma \rightarrow 1} \left( C - C - \ln t|_{\beta(\gamma-1)}^1 + \ln t|_{(\alpha+\beta)(\gamma-1)}^1 \right) \quad (57)$$

simplifying:

$$\begin{aligned} T_0^{(-)}(\alpha, \beta) &= \frac{e^{-\alpha}}{\alpha} \lim_{\gamma \rightarrow 1} (\ln[\beta(\gamma-1)] - \ln[(\alpha+\beta)(\gamma-1)]) \\ &= \frac{e^{-\alpha}}{\alpha} \lim_{\gamma \rightarrow 1} (\ln \beta + \ln(\gamma-1) - \ln(\alpha+\beta) - \ln(\gamma-1)) \end{aligned} \quad (58)$$

we finally get for  $T_0^{(-)}(\alpha, \beta)$  a simple expression:

$$T_0^{(-)}(\alpha, \beta) = \frac{e^{-\alpha}}{\alpha} \ln \left( \frac{\beta}{\alpha+\beta} \right) \quad (59)$$

Now we consider the  $n$ th-term:

$$\begin{aligned} T_n^{(-)}(\alpha, \beta) &= (-1)^n \frac{d^n}{d\alpha^n} T_0^{(-)}(\alpha, \beta) = (-1)^n \frac{d^n}{d\alpha^n} \frac{e^{-\alpha}}{\alpha} \ln \left( \frac{\beta}{\alpha+\beta} \right) \\ &= (-1)^n \frac{d^n}{d\alpha^n} \left[ A_0(\alpha) \ln \left( \frac{\beta}{\alpha+\beta} \right) \right] \\ &= (-1)^n \sum_{m=0}^n C_m^n \frac{d^{n-m}}{d\alpha^{n-m}} A_0(\alpha) \frac{d^m}{d\alpha^m} \ln \left( \frac{\beta}{\alpha+\beta} \right) \end{aligned} \quad (60)$$

obtaining finally:

$$T_n^{(-)}(\alpha, \beta) = A_n(\alpha) \ln \left( \frac{\beta}{\alpha+\beta} \right) + \sum_{m=1}^n C_m^n \frac{(m-1)!}{(\alpha+\beta)^m} A_{n-m}(\alpha) \quad (61)$$

where  $A_n(\alpha)$  is the Mulliken integral:

$$A_n(\alpha) = \int_1^\infty t^n e^{-\alpha t} = \frac{n! e^{-\alpha}}{\alpha^{n+1}} \sum_{k=0}^n \frac{\alpha^k}{k!}. \quad (62)$$

In Table 1, the pattern of convergence of the three-center overlap integral is shown. To obtain a convergence of 15 decimal digits 19 terms of the expansion are needed. To obtain 30 decimal digits accuracy, about 30 terms of the expansion are required. These values have been calculated with Maple [30]. This algorithm will be programmed in a Fortran source code and the efficiency of the calculation of the integral can be tested. Further, this integral will be tested by comparing the two-electron three-center integrals with the values obtained by the SMILES computer code [31] version which uses the Gaussian expansion method.

In Table 2, a number of three-center one-electron integrals for different exponents, quantum numbers and interatomic distances is presented, with respect to the number of terms necessary in the expansion.

### 3.2 Summary

The three-electron overlap pone-electron integral is:

$$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R) = \frac{1}{N!} \sum_{k=0}^{n_b+n_c} \sum_{u=0}^{n_a+k} \sum_{s=0}^N \frac{\pi N!}{2^{n_a+n_b+n_c+k-1} s!} D_k^{n_b n_c} D_u^{n_a k} \left( \frac{\beta - \gamma}{2} \right)^s \\ \times B_{n_b+n_c-k, s+u; n_a+k-2u-s-1} \left( \alpha, \frac{(\beta + \gamma)}{2} \right), \quad (63)$$

The auxiliary integrals for postive and negative  $k$ :

$$B_{nm;+k}(\alpha, \beta) = \sum_{h=0}^k \frac{k!}{(h-k)!} \beta^{-h-1} (e^\beta A_{n;m,m+k-h}(\alpha + \beta) - e^{-\beta} A_{n;m+k-h,m}(\alpha + \beta)) \quad (64)$$

$$B_{nm;-k}(\alpha, \beta) = \frac{(-\beta)^{k-1}}{(k-1)!} \sum_{i=0}^m (-1)^i C_i^m \left[ T_{n+2m-2i}^{(+)}(\alpha, \beta) - T_{n+2m-2i}^{(-)}(\alpha, \beta) \right] \\ - \sum_{h=1}^{k-1} \frac{(k-h-1)!}{(k-1)!} (-\beta)^{h-1} [e^{-\beta} A_{n;m-k+h,m}(\alpha + \beta) - e^\beta A_{n;m,m-k+h}(\alpha + \beta)] \quad (65)$$

The auxiliary functions:

$$T_n^{(+)}(\alpha, \beta) = A_n(-\alpha) Ei(-2\beta) + (-1)^n A_n(-\alpha) Ei(-2(\alpha + \beta)) \\ - \sum_{m=1}^n (-1)^{n-m} 2^m C_m^n A_{n-m}(-\alpha) (-1)^{m-1} A_{m-1}(2(\alpha + \beta)) \quad (66)$$

$$T_n^{(-)}(\alpha, \beta) = A_n(\alpha) \ln \left( \frac{\beta}{\alpha + \beta} \right) + \sum_{m=1}^n C_m^n \frac{(m-1)!}{(\alpha + \beta)^m} A_{n-m}(\alpha) \quad (67)$$

The one-electron auxiliary integrals:

$$A_n(\alpha) = \int_1^\infty t^n e^{-\alpha t} = \frac{n! e^{-\alpha}}{\alpha^{n+1}} \sum_{k=0}^n \frac{\alpha^k}{k!}, \quad (68)$$

$$A_{n;mk}(\alpha) = \sum_{j=0}^{m+k} D_j^{mk} A_{n+m+k-j}(\alpha). \quad (69)$$

## 4. Two-electron three-center integrals

There are several kinds of two-electron integrals where three centers are involved, see Figure 1: Coulomb-exchange (the first two) and hybrid-exchange (the last two):

$$\begin{aligned}
[aa, bc] &= \int \int \chi_a(1) \chi_a(1) \frac{1}{r_{12}} \chi_b(2) \chi_c(2) d\tau_1 d\tau_2, \\
[bb, ac] &= \int \int \chi_b(1) \chi_b(1) \frac{1}{r_{12}} \chi_a(2) \chi_c(2) d\tau_1 d\tau_2, \\
[ab, ac] &= \int \int \chi_a(1) \chi_b(1) \frac{1}{r_{12}} \chi_a(2) \chi_c(2) d\tau_1 d\tau_2, \\
[ab, bc] &= \int \int \chi_a(1) \chi_b(1) \frac{1}{r_{12}} \chi_b(2) \chi_c(2) d\tau_1 d\tau_2.
\end{aligned} \tag{70}$$

The Coulomb exchange integrals can be evaluated by integration over the coordinates of electron 1 [32], obtaining a linear combination of three-center overlap integrals calculated in this paper:

In general a two-electron integral can be written:

$$[aa, bc] = \int_0^\infty dr_2 \int_{r_2}^\infty \chi_a(1) \chi_a(1) \hat{g}_{12} \chi_b(2) \chi_c(2) d\tau_1 d\tau_2, \tag{71}$$

where  $\hat{g}_{12}$  is an operator of  $r_1$  and  $r_2$ . For  $L = 0$  the operator is  $\hat{g}_{12} = g_{12}$  where  $g_{12}$  means the largest of  $r_1$  and  $r_2$ . There are two integration domains:  $r_1 < r_2$  and  $r_1 > r_2$ . One may refer the interelectronic distance  $r_{12}$  to center  $a$  and expand it in terms of the variables  $r_{1a}$  and  $r_{2a}$ :

$$\begin{aligned}
[aa, bc] &= \int_0^\infty dr_1 \int_{r_{1a}}^\infty \chi_a(1) \chi_a(1) \frac{1}{r_2} \chi_b(2) \chi_c(2) dr_{2a} + \int_0^\infty dr_{2a} \int_{r_{2a}}^\infty \chi_a(1) \chi_a(1) \frac{1}{r_{1a}} \chi_b(2) \chi_c(2) dr_{1a} \\
&= \int_0^\infty dr_{2a} \int_0^{r_{2a}} \chi_a(1) \chi_a(1) \frac{1}{r_{2a}} \chi_b(2) \chi_c(2) dr_{1a} + \int_0^\infty dr_{2a} \int_{r_{2a}}^\infty \chi_a(1) \chi_a(1) \frac{1}{r_{1a}} \chi_b(2) \chi_c(2) dr_{1a}.
\end{aligned} \tag{72}$$

As these orbitals are located at the same center, we can integrate over the coordinates of one-electron [32]:

$$A_n(x, \alpha) = \int_x^\infty r_{1a}^n e^{-\alpha r_{1a}} dr_{1a} = e^{-\alpha x} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{x^{n-k}}{\alpha^{k+1}}, \tag{73}$$

$$U_n(x, \alpha) = \int_0^x r_{1a}^n e^{-\alpha r_{1a}} dr_{1a} = A_n(\alpha) - A_n(x, \alpha) = \frac{n!}{\alpha^{n+1}} - e^{-\alpha x} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{x^{n-k}}{\alpha^{k+1}}. \tag{74}$$

The Coulomb-exchange integrals of Eq. (70) can be evaluated integrating over the coordinates of electron 1, writting them explicitly:  $n_{1a} = n_1 + n'_1 - 1$  and  $\zeta = \zeta_1 + \zeta'_1$ :

$$\begin{aligned}
[aa, bc] &= 4\pi \int r_{2b}^{n_b-1} e^{-\zeta_b r_{2b}} r_{2c}^{n_c-1} e^{-\zeta_c r_{2c}} d\tau_2 \int r_{1a}^{n_a-1} e^{-\zeta_a r_{1a}} \frac{1}{r_{12}} r_{1a}^2 dr_{1a}, \\
[bb, ac] &= 4\pi \int r_{2a}^{n_a-1} e^{-\zeta_a r_{2a}} r_{2c}^{n_c-1} e^{-\zeta_c r_{2c}} d\tau_2 \int r_{1b}^{n_b-1} e^{-\zeta_b r_{1b}} \frac{1}{r_{12}} r_{1b}^2 dr_{1b},
\end{aligned} \tag{75}$$

using Eqs. (73) and (74) we obtain

$$[aa, bc] = 4\pi \int_0^\infty r_{2b}^{n_b-1} e^{-\zeta_b r_{2b}} r_{2c}^{n_c-1} e^{-\zeta_c r_{2c}} d\tau_2 \left\{ \frac{1}{r_{2a}} \int_0^{r_{2a}} r_{1a}^{n_a+1} e^{-\zeta_a r_{1a}} dr_{1a} + \int_{r_{2a}}^\infty r_{1a}^{n_a} e^{-\zeta_a r_{1a}} dr_{1a} \right\}, \quad (76)$$

$$[aa, bc] = 4\pi \int_0^\infty r_{2b}^{n_b-1} e^{-\zeta_b r_{2b}} r_{2c}^{n_c-1} e^{-\zeta_c r_{2c}} d\tau_2 \left\{ \frac{1}{r_{2a}} \frac{(n_a+1)!}{\zeta_a^{n_a+2}} - \frac{e^{-\zeta_a r_{2a}} (n_a+1)!}{r_{2a} \zeta_a^{n_a+2}} \right. \\ \left. - \sum_{k=0}^{n_a+1} \frac{(n_a+1)!}{(n_a+1-k)! \zeta_a^{k+1}} r_{2a}^{n_a-k} e^{-\zeta_a r_{2a}} + \sum_{k=0}^{n_a} \frac{(n_a)!}{(n_a-k)! \zeta_a^{k+1}} r_{2a}^{n_a-k} e^{-\zeta_a r_{2a}} \right\}, \quad (77)$$

$$[aa, bc] = 4\pi \int_0^\infty r_{2b}^{n_b-1} e^{-\zeta_b r_{2b}} r_{2c}^{n_c-1} e^{-\zeta_c r_{2c}} d\tau_2 \left\{ \frac{1}{r_{2a}} \frac{(n_a+1)!}{\zeta_a^{n_a+2}} (1 - e^{-\zeta_a r_{2a}}) \right. \\ \left. + \sum_{k=0}^{n_a} \frac{k-1}{(n_a+1-k)(n_a-k)! \zeta_a^{k+1}} (n_a)! r_{2a}^{n_a-k} e^{-\zeta_a r_{2a}} \right\}. \quad (78)$$

Finally the Coulomb-exchange reulsion integral is expressed as a linear combination of three-center overlap integrals defined in Eq. (4):

$$[aa, bc] = 4\pi \frac{(n_a+1)!}{\zeta_a^{n_a+2}} (S_{0,n_b,n_c}(0, \zeta_b, \zeta_c, R) - S_{0,n_b,n_c}(\zeta_a, \zeta_b, \zeta_c, R)) \\ + 4\pi \sum_{k=0}^{n_a} \frac{k-1}{(n_a+1-k)(n_a-k)! \zeta_a^{k+1}} \frac{n_a!}{\zeta_a^{k+1}} S_{n_a-k+1,n_b,n_c}(\zeta_a, \zeta_b, \zeta_c, R), \quad (79)$$

where the integral  $S_{0,n_b,n_c}(0, \zeta_b, \zeta_c, R)$  is the three-center nuclear attraction integral defined in Ref. [33]:

$$S_{0,n_b,n_c}(0, \zeta_b, \zeta_c, R) = K_{na,nb,nc} = \int \frac{\chi_b \chi_c}{r_a} d\tau \quad (80)$$

$S_{0,n_b,n_c}(\zeta_a, \zeta_b, \zeta_c, R)$  should be analyzed. Anagously for  $[bb, ac]$  we obtain:

$$[bb, ac] = 4\pi \frac{(n_b+1)!}{\zeta_b^{n_b+2}} (S_{0,n_a,n_c}(0, \zeta_a, \zeta_c, R) - S_{0,n_a,n_c}(\zeta_b, \zeta_a, \zeta_c, R)) \\ + 4\pi \sum_{k=0}^{n_b} \frac{k-1}{(n_b+1-k)(n_b-k)! \zeta_b^{k+1}} \frac{n_b!}{\zeta_b^{k+1}} S_{n_b-k+1,n_a,n_c}(\zeta_b, \zeta_a, \zeta_c, R) \quad (81)$$

$S_{0,n_a,n_c}(0, \zeta_a, \zeta_c, R)$  are expressed as:

$$S_{0,n_a,n_c}(0, \zeta_a, \zeta_c, R) = K_{nb,nanc} = \int \frac{\chi_a \chi_c}{r_b} d\tau \quad (82)$$

The integral  $S_{0,n_a,n_c}(\zeta_b, \zeta_a, \zeta_c, R)$  is an especial case of overlap integral with  $n_a = -1$  and should be treated separately, as Eqs. (9-14) are derived for  $n_a \geq 1$ .

Next we will calculate some two-electron integrals and compare with the literature values and values obtained with a computer program by Rico *et al.* [31] using the Gaussian expansion method.

## Conclusions

In this paper three-center overlap integrals are calculated, which are used to calculate the two-center three-center repulsion integrals. The integrals consist of an expansion which converges relatively fast.

## Acknowledgments

One of us (T. Ö.) would like to thank the Deutsche Forschungsgemeinschaft and TUBITAK for a grant to visit Erlangen for three months. The authors are very indepted to Prof. Peter Otto for encouraging this project.

## Appendix A

In Figure 2 the symmetric triangular conformation of the centers is shown. The interelectronic distances are equal  $R = R_{ab} = R_{ac}$ . The elliptical coordinates of the center  $a$  with respect to the focii  $b, c$  are fixed values:

$$\mu_a = \frac{R_{ab} + R_{ac}}{R} = 2, \quad \nu_a = 0, \quad (\text{A.1})$$

and the relation:

$$\cos(\phi_1 - \phi_a) = \cos \phi_1 \cos \phi_a + \sin \phi_1 \sin \phi_a \quad (\text{A.2})$$

independently of the choose of the angle  $\phi_a$ , in integrations over  $s$ -type Slater the integrals  $\int_0^{2\pi} \cos \phi_1 d\phi_1 = 0$  and  $\int_0^{2\pi} \sin \phi_1 d\phi_1 = 0$  vanish. Then we have:

$$r_{1a}^2 = \frac{R^2}{4}(\mu_1^2 + \nu_1^2 + 2) \quad (\text{A.3})$$

and therefore

$$r_{1a} = \frac{R}{2}(\mu_1^2 + \nu_1^2 + 2)^{1/2}, \quad (\text{A.4})$$

accordingly the substitution in this case is:

$$t = (\mu^2 + \nu^2 + 2)^{1/2} + \nu. \quad (\text{A.5})$$

which is similar to the one used in Section 1, and therefore the steps of integration described in previous Sections can be used. The triangular conformation is very important because it is the ground state conformation of the  $\text{H}_3$  molecule and many molecular systems.

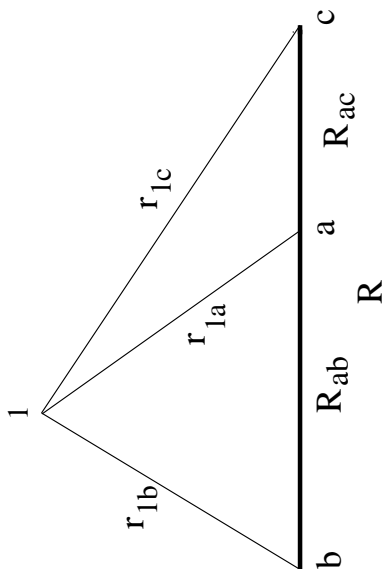
## References

- [1] J. C. Slater, Phys. Rev. **31** 333 (1928).
- [2] S. F. Boys, Proc. Roy. Soc. (London), **A200**, 542 (1950).
- [3] Milan Randic, Tallahassee, Florida 1981. *ETO multicenter integrals*, C. A. Weatherford and H. Jones eds. Dortdrecht, p. 141, 1982.
- [4] J. S. Sims and S. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).
- [5] D. C. Clary, *Hylleraas-type wave functions for atoms and diatomic molecules*, Cambridge, England, 1977.
- [6] R. S. Mulliken and C. C. Roothaan, Proc. Natl. Acad. Sci. (U.S.) **45**, 394 (1959).
- [7] M. P. Barnett and C. A. Coulson, Phil. Trans. A **243**, 221 (1951).
- [8] P. O. Löwdin, Adv. Phys. **5**, 1 (1956).
- [9] F. E. Harris and H. H. Michels, J. Chem. Phys. **43**, S165 (1965).
- [10] I. I. Guseinov, Phys. Rev. A **22**, 369 (1980).
- [11] Y. G. Smeyers, Theoret. chim. Acta (Berl.) **4**, 452 (1966).
- [12] J. Fernández Rico, R. López, I. Ema and G. Ramírez, J. Comp. Chem. **26**, 846 (2005).
- [13] J. Fernández Rico, R. López, I. Ema and G. Ramírez, Int. J. Quantum Chem. **108**, 1415 (2008).
- [14] J. Fernández Rico, R. López, I. Ema and G. Ramírez, Comp. Phys. Comm. **105**, 216 (1997).
- [15] I. Shavitt and M. Karplus, J. Chem. Phys. **36**, 550 (1962).
- [16] L. Berlu, H. Safouhi, and P. Hoggan, Int. J. quantum Chem. **99**, 221 (2004).
- [17] J. C. Cesco, J. E. Pérez, C. C. Denner, G. O. Giubergia, A. E. Rosso, Appl. Numer. Math. **55**, 173 (2005).
- [18] E. Filter and E. O. Steinborn, Phys. Rev. A **18**, 1 (1978).
- [19] H. Tai, J. Phys. B: Atom. Molec. Phys. **12**, 177 (1979).
- [20] E.J. Weniger, E.O. Steinborn, J. Chem. Phys. **78**, 6121 (1983).
- [21] H. Safouhi and P. E. Hoggan, J. Phys. A **32**, 6203 (1999).
- [22] S. Duret, A. Bouferguene, H. Safouhi, J. Comp. Chem. **29**, 934 (2008).
- [23] D. Antolovic and H. J. Silverstone, Int. J. Quantum Chem. **100**, 146 (2004).



- [24] Volume in Memory of H. W. Jones, Eds. P. E. Hoggan and C. A. Weatherford, *Int. J. Quantum Chem.* **100**, 2004.
- [25] *Recent Advances in Computational Chemistry: Molecular Integrals over Slater Orbitals*, Eds. T. Özdoğan and M. B. Ruiz, Transworld Research Network, Kerala, India, 2008.
- [26] J. O. Hirschfelder, H. Eyring and N. Rosen, *J. Chem. Phys.* **4**, 121 (1936).
- [27] J. O. Hirschfelder and C. N. Weygandt, *J. Chem. Phys.* **6**, 806 (1938).
- [28] N. Rosen, *Phys. Rev.* **38**, 255 (1931).
- [29] I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products*, Academic Press, New York, 1965.
- [30] MAPLE 9 Release by Waterloo Maple Inc. Copyright 2003.
- [31] J. Fernández Rico, R. López, I. Ema, and G. Ramírez, *J. Comp. Chem.* **25**, 1987, (2004).
- [32] K. Peuker, PhD Thesis, *Highly accurate calculation of molecular integrals using Slater orbitals. CI calculations on BeH<sub>2</sub>*, University Erlangen-Nürnberg, 2008.
- [33] K. Peuker and M. B. Ruiz, *J. Math. Chem.* **43**, 701 (2007).

Figure 1



**Figure 1:** Definition of the coordinates of one electron with respect to three centers: linear conformation.

**Figure 2:** Definition of the coordinates of one electron with respect to three centers: triangular conformation.

**Table 1:** Convergence pattern of the three-center overlap integral for the orbital parameters  $n_a = 1$ ,  $n_b = 2$ ,  $n_c = 1$  and  $\zeta_a = 1.6$ ,  $\zeta_b = 1.4$ ,  $\zeta_c = 1.2$ ;  $R = 1.4$  a.u.

1	-0.11416
2	-0.12293 3
3	-0.12160 22
4	-0.12219 350
5	-0.12207 7743
6	-0.12210 04107
7	-0.12209 67757 3
8	-0.12209 73204 83
9	-0.12209 72448 624
10	-0.12209 72547 7065
11	-0.12209 72535 25580
12	-0.12209 72536 75642 0
13	-0.12209 72536 58049 61
14	-0.12209 72536 60052 409
15	-0.12209 72536 59828 9497
16	-0.12209 72536 59853 35836
17	-0.12209 72536 59850 73400 8
18	-0.12209 72536 59851 01158 63
19	-0.12209 72536 59850 98261 802
20	-0.12209 72536 59850 98559 9711
21	-0.12209 72536 59850 98529 65861
22	-0.12209 72536 59850 98532 70074 8
23	-0.12209 72536 59850 98532 39925 80
24	-0.12209 72536 59850 98532 42873 615
25	-0.12209 72536 59850 98532 42589 4768
26	-0.12209 72536 59850 98532 42616 42719
27	-0.12209 72536 59850 98532 42613 91777
28	-0.12209 72536 59850 98532 42614 14624
29	-0.12209 72536 59850 98532 42614 12602
30	-0.12209 72536 59850 98532 42614 12774

**Table 2:** Three-center overlap integrals.  $N$  is the number of terms of the expansion needed to calculate accurately the printed number of decimal digits.

$n_a$	$n_b$	$n_c$	$\zeta_a$	$\zeta_b$	$\zeta_c$	$R$	$S_{n_a n_b n_c}(\zeta_1, \zeta_b, \zeta_c, R)$	$N$
1	1	1	1.3	1.3	1.3	1.0	-0.10852 96351 53609 38988	25
1	1	1	1.1	1.3	1.5	1.0	-0.41057 77481 70340 63986	26
1	2	2	2.0	2.0	2.0	2.0	0.00409 87551 44074 883	30
2	2	2	1.6	1.4	1.4	2.5	0.08943 10170 26917 0505	28
4	3	2	2.6	2.4	1.6	3.0	0.00362 95811 14392 3873	25

Figure 2

